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**Effect of dispersant on nano-PTFE based lubricants
on tribo-performance in fretting wear mode**

Mukesh Kumar Dubey^{1,2}, Jayashree Bijwe^{2*}, S.S.V. Ramakumar¹

¹Indian Oil Corporation Ltd., R & D Centre, Faridabad, India, ²Indian Institute of Technology, Delhi, India.

*author for correspondence: jbijwe@gmail.com

Abstract

Very recently nano-PTFE particles have shown great promise as anti-friction (AF), anti-wear (AW) and extreme pressure (EP) additive. However, its stability in oil in suspension form was limited and the issue needed immediate attention. Hence, proper dispersant was required to be tried, which could avoid sedimentation and agglomeration problem of NPs for a longer time. Hence polyisobutylene succinimide (PIBSI) was selected as a dispersant in this work. This paper describes the effect of nano-PTFE- PIBSI additive interaction in a lubricant system. Initially few oils were prepared containing various amounts (1, 5 and 10 %) of PIBSI to investigate its influence on extent of stability and influence on tribo-properties leading to selection of an optimum amount for best possible combination of properties. Oils with PIBSI in fixed amount (1 %) and varying amount of nano-PTFE particles (0 to 6 wt %) were then prepared. The oils were characterized for physical properties such as density, viscosity, pour point and flash point. The friction and wear studies performed in the oscillating wear mode indicated that PIBSI 1 % (wt) was an optimum amount. However, PIBSI-NP combination clearly showed competition as AF and AW additive and film forming tendency on the counterface and hence, antagonistic behaviour. With increase in amount of NPs, the dominance of NPs increased and finally combination of PIBSI and NPs (6 wt %) could significantly improve the AF property (35 %) as well as AW property (25 %) of the virgin oil besides improving the stability of suspension significantly.

The topography and surface chemistry of the specimens were examined using scanning electron microscopy/ atomic force microscopy to establish the nature of protective surface film formed on the steel surfaces.

Keywords: nano-PTFE in oil, nano-lubricant, dispersant, PIBSI dispersant, fretting wear mode, surface analysis

1.0 Introduction

Additives in lubricating oils to reduce friction and wear of surfaces in dynamic contact is always of topical interest. Wear protection is extremely important to the industry from mechanical maintenance and economic point of view. In the case of sliding elements, extreme pressure (EP) additives are extensively used in hypoid gears, metal cutting and metal forming operations.

Solid lubricants such as Molybdenum disulphide (MoS_2), Graphite, Polytetrafluoroethylene (PTFE) etc. are used in oils primarily as extreme pressure (EP) or anti-wear (AW) or anti-friction (AF) types of additives [1, 2]. PTFE has un-branched chain-like molecular structure and weak Van der Waals forces between aligned PTFE molecules which result in low μ and wear due to thin, coherent and uniform transfer film on the rubbing surfaces [3, 4]. The use of nanoparticles (NPs) as solid lubricants in oils is a comparatively recent concept. When a particle is fragmented into NPs, its reactivity increases. Smaller the particle size, higher is the surface area. NPs have a very high surface area to volume ratio, due to which more number of atoms can interact with other surfaces. NPs are considered as potential additives in lubricant mainly as AF, AW or EP. [5-15].

In our earlier studies [16, 17], PTFE based micro-lubricant (MLs) and nano-lubricant (NLs) with varying sizes were prepared in API Group II lubricating base oil. The approx. particle sizes were; 50 nm, 150 nm, 400 nm and 12 μm , and the particle concentrations were 4, 8 and 12 wt %. They were characterised for physical and tribological properties. Significantly improved tribo-performance (EP, AW and AF) was reported due to inclusion of PTFE particles especially due to NPs. The paper also dealt with the optimum amount of nano-PTFE required for best performance properties of NP-oils and the detailed mechanism behind the

observed improvements. However, these studies were based on exploration of PTFE NPs in oil, without any dispersant. Owing to the requirement of long standing stability of finished lubricants, it was thought worthwhile to incorporate appropriate dispersants to improve the storage stability of nano-PTFE dispersion in oil. Since dispersant being long chain molecules with considerable surface activity, it is pertinent to investigate the impact of these dispersants on overall tribological performance of nano- PTFE dispersion apart from the stability.

The tribological benefits obtained due to nano-sized Inorganic Fullerene like molybdenum disulfide (IF-MoS₂) was reported to be lost in the presence of succinimide based dispersants [18]. Aralihali and Biswas [19] selected a range of dispersants (on the basis of their polar moieties) to suspend nano- MoS₂ particles in an industrial lubricating oil. They reported that the presence of dispersant led to efficient de-agglomeration of NPs, which in turn resulted in reduction in μ from 0.080 to 0.035.

Literature indicates that although PTFE is a very promising solid lubricant mainly for composites and also for oils and greases, no papers could be available for exploring nano-PTFE as an additive in oil except our own work. Such type of study becomes more important when nano-PTFE is already reported as very promising nano-particles in high performance polymer composites [20].

In view of the above, current paper reports on the results of NP-oils, prepared with different concentrations of nano-PTFE particles (0 to 6 wt %) along with a selected dispersant and related tribo-data generated in fretting motion. Since the work is a stage ahead of an earlier work, some data from previous paper had to be added for comparison.

2. Materials and Methodology

2.1 Selection of Material

2.1.1 Selection of Nano-PTFE particles

Nano PTFE powder was selected to formulate the nano-lubricants. The powder (30-50 nm in size) was procured from Shanghai SMEC Trading Co. China. Field emission scanning electron micrograph (FESEM), (ZEISS, Supra 55)} of nano PTFE particles are shown in Fig. 1 [20].

2.1.2 Base- oil Selected

Same base oil used in earlier studies (150 N Group II base oil) was selected as a base-stock for the studies. This parent oil (designated as O_p) was used for preparing various NP-oils based on different concentrations of two types of the selected additives viz. nano-PTFE and a dispersant PIBSI.

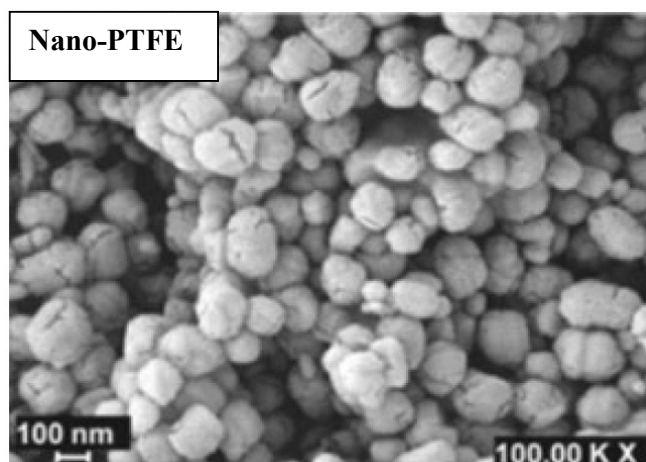


Figure 1- High resolution FESEM micrographs of nano-PTFE particles appears as 70-100 nm from the micrograph [20]. (The figure is reproduced with kind permission from Springer.

2.1.3 Selection of Dispersant

Lubricants need to be very stable under diverse temperature conditions and should not precipitate/ sediment the solid particles. Dispersants are usually ashless (non metallic) organic chemicals. They generally keep contaminants and by products dispersed in the oil.

They help to prevent the formation of deposits during oil usage. Dispersants prevent filter blockage and varnishes metal surface. In this research work, however, they are added with an objective of stabilizing and keeping NPs in a suspension mode. The instability of suspensions is mainly due to aggregation and sedimentation of particles.

Polyisobutylene Succinimide (PIBSI) was used as a dispersant in the present study and its typical properties are shown in Table 1 while structure is shown in Fig. 2

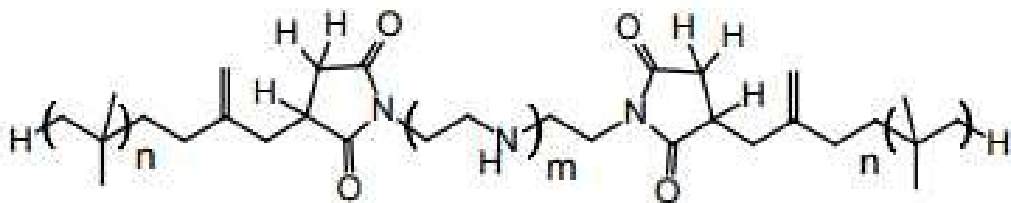


Figure 2- Chemical structure of Polyisobutylene Succinimide (PIBSI).

Table 1- Properties of selected dispersant

Properties	
Kinetic viscosity (KV) @ 100 °C, cSt	250
Flash point, °C PMCC	145
TBN, mg KOH/gm	12
Nitrogen, % wt	0.99
Specific gravity @ 15.6 °C	0.918
Polymeric component (% wt)	45
Mol. wt. of polymeric component	3317

2.2 Preparation of NP-oils

NP-oils based on different concentrations of nano-PTFE and dispersant were developed using probe sonication technique and the details are discussed in our earlier paper [16]. Details of nano-PTFE powder along with designations of prepared NP-oils are shown in Table 2. It was also important to examine if the dispersant also contributes to the tribo-performance of oils. Hence three oils containing 1, 5 and 10 % dispersant were also developed.

Table 2- Details of oils developed in the earlier work [17] and in the present work.

Sl. No.	Concentration (wt %) and type of additive used in parent oil		Designations of oils	Ref.
	Nano-PTFE	Dispersant		
1	0 %	0 %	O _P	[17]
2	1 %	0 %	O _{N1}	
3	2 %	0 %	O _{N2}	
4	3 %	0 %	O _{N3}	
5	4 %	0 %	O _{N4}	
6	5 %	0 %	O _{N5}	
7	6 %	0 %	O _{N6}	
8	0 %	1 %	O _D	
9	1 %	1 %	O _{DN1}	
10	2 %	1 %	O _{DN2}	
11	3 %	1 %	O _{DN3}	
12	4 %	1 %	O _{DN4}	
13	5 %	1 %	O _{DN5}	
14	6 %	1 %	O _{DN6}	
15	0 %	5 %	O _{D5}	
16*	0 %	10 %	O _{D10}	

Oils from 8-16 were prepared for work in this paper.

2.3 Characterization of Oils

The oils, thus prepared were characterized in details for physical properties as shown in Table 3a (oils with increasing amount of dispersant) and 3b (fixed amount of dispersant and increasing amount of nano-PTFE) respectively.

Table 3a: Physical properties of developed oils with increasing amount of dispersant.

Parameter/instrument/method		O _P	O _D	O _{D5}	O _{D10}
1	Density (g/cm ³) at 15.5 °C (Anton Paar DMA-4100) ASTM D 1298	0.846	0.847	0.848	0.850
2	Kinematic Viscosity (cSt) 40 °C	29.56	30.68	32.67	35.61

	(Cannon CAV-2000) ASTM D-445	100 ^o C	5.177	5.329	5.637	6.03
3	Viscosity Index ASTM D-2270		104.31	106.31	111.51	114.7
4	Pour Point (^o C)		-24	-33	-27	-27
	(LAWLER DR4-11) ASTM D-97					
5	Flash Point (^o C)		227	235	236	237
	(Tanaka ACO-T602) ASTM D-92					

Table 3b: Physical properties of developed oils containing 1 % PIBSI and increasing amount of nano-PTFE.

Parameter/instrument/method	O _P	O _D	O _{DN1}	O _{DN2}	O _{DN3}	O _{DN4}	O _{DN5}	O _{DN6}
1 Density (g/cm ³) at 15.5 ^o C (Anton Paar DMA-4100) ASTM D 1298	0.846	0.847	0.851	0.856	0.861	0.866	0.871	0.877
2 Kinematic 40 ^o C	29.56	30.68	30.94	31.63	32.36	33.12	34.09	40.25
Viscosity (cSt) 100 ^o C (Cannon CAV-2000) ASTM D-445	5.177	5.329	5.368	5.454	5.535	5.624	5.751	6.431
3 Viscosity Index ASTM D-2270	104.3	106.3	106.97	107.63	107.7	108.07	109.19	109.54
Pour Point (^o C) (LAWLER DR4-11) ASTM D-97	-24	-33	-33	-33	-30	-30	-27	-27
5 Flash Point (^o C) (Tanaka ACO-T602) ASTM D-92	227	235	231	231	231	231	237	243

As seen from Table 3a, addition of dispersant provided a marginal increase in the density, viscosity (at both temperatures) and VI of oil. Pour point also decreased but not uniformly. Flash point temperature also increased due to inclusion of dispersant sharply from 227^oC (for O_P) to 235 ^oC for O_D, with further marginal increase for remaining oils.

From the Table 3b, it was observed that trends were similar due to addition of NPs. Increase in the amount of NPs led to a marginal increase in the density, viscosity (at both

temperatures) and VI of oil. Pour point also decreased almost regularly due to addition of dispersant with an exception of O_{D5}, which showed sudden drop (-33 °C). Flash point temperature showed irregular trends.

2.4 Tribo- performance of Oils

An Optimol-SRV-III oscillating friction and wear tester was employed to examine the tribological properties of developed oils. The friction test was conducted in a reciprocating “ball-on-block” mode, by oscillating an AISI 52100 steel ball (diameter 10 mm) over an AISI 52100 steel block (ϕ 24 mm × 7.9 mm) where a drop of oil was placed in the beginning of experiment. The tribo- pair was thoroughly rinsed with petroleum ether prior and after the test. The operating conditions were: frequency 50 Hz, stroke length 1 mm, duration of the test 60 min and load 100 N. The total distance fretted was 360 meters. The contact pressure was 2.19 GPa. 0.3 mL of lubricant was used in each test and the average reading of three tests was considered to plot the graphs. After the completion of the test, the steel discs were cleaned with petroleum ether (40-60 °C) prior to the investigations of worn surfaces.

2.5 Worn Surface Analysis

Atomic force microscope (AFM, Park Systems XE-70) and SEM were used for surface morphological study. AFM images give three dimensional (3D) topographic features. The topography of worn steel disc was studied with AFM. AFM measurements were carried out in contact mode with silicon nitride cantilevers.

Energy dispersive X ray analysis spectra (EDAX) were obtained with Thermo Electron Corporation model C10017 system to examine the chemical features and elemental compositions of the tribo-film generated on the worn surfaces.

3.0 Results and Discussions

3.1 Stability Studies on Oil Suspensions- Visual Inspection

The photographs of the parent oil and dispersant added oils with and without PTFE are shown in Fig. 3 (i and ii). The NP-oils were kept for 45 days after sonication. All dispersant added nano- PTFE particles remained dispersed in the parent oils and hardly any sedimentation of NPs was observed even after 63 days, contrary to our earlier studies [16,17], where stability of nano-suspension without dispersant was reported as 15 days. However, minute inspection indicated that after 63 days initiation of sedimentation had started and higher the amount of dispersant, lower was the tendency.

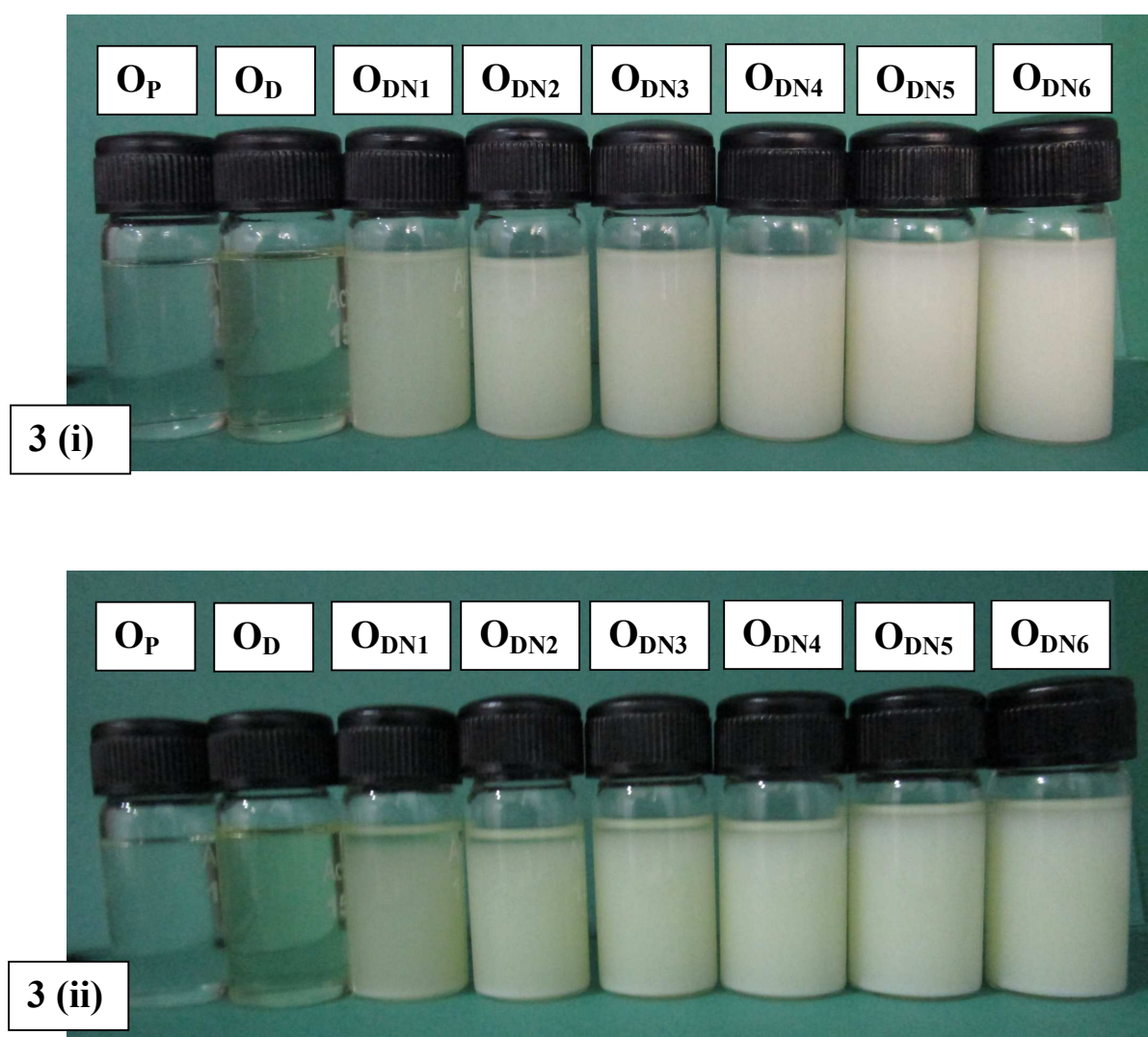


Figure 3 – Stable suspensions of O_P , O_D , O_{DN1} , O_{DN2} , O_{DN3} , O_{DN4} , O_{DN5} and O_{DN6} ;

(i) Observed after 45 days and (ii) after 63 days

3.2 Stability Studies on Oil Suspensions- DLS (Dynamic light scattering)

Two samples O_{N6} and O_{DN6} were selected as representative samples to study the effect of dispersant on the suspension stability. The particle size distribution of the samples was analysed based on the principle of dynamic light scattering (DLS) with Zetasizer Nano ZS 90, Malvern Instruments UK. The NP-oils sample was first diluted with petroleum ether (40-60°C) (oil to ether vol. ratio-7:3). The sample was injected slowly in the polystyrene cuvette to avoid air bubbles. The cuvette was placed into the Zetasizer and equilibrated at 25 °C for 120 seconds prior to the particle size measurements. Three repeat readings on each sample were taken and average value was considered.

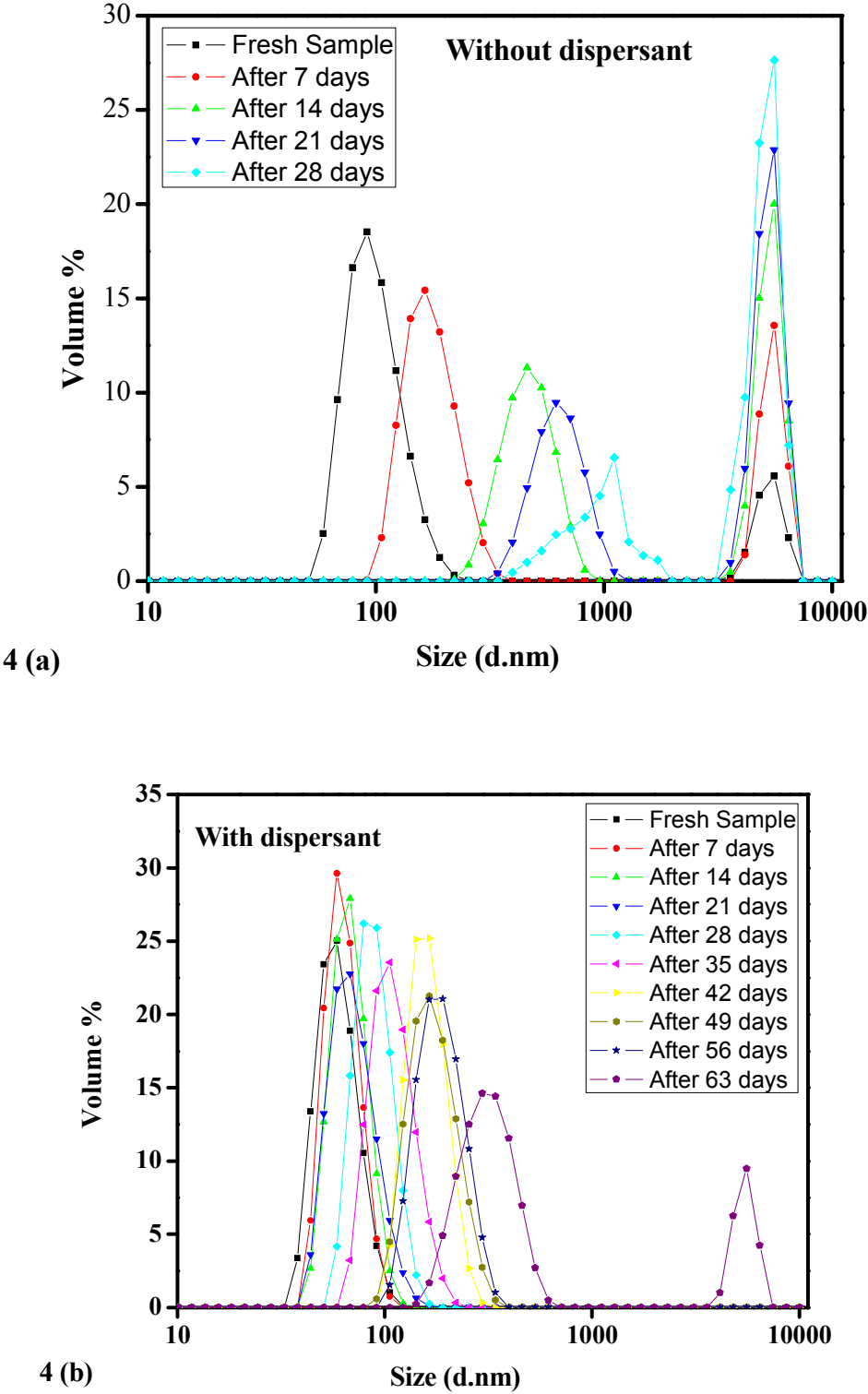


Figure 4 – Comparison of particle size distribution as a function of time for (a) O_{D6} and (b) O_{DN6} (DLS studies).

Table 4- Size distribution of NPs with dispersant by volume for O_{DN6} and O_{N6} (DLS studies)

O _{N6}						O _{DN6}				
Days	Z-Ave (d.nm)	Peak	Size (d.nm)	% Vol	St. Dev	Z-Ave (d.nm)	Peak	Size (d.nm)	% Vol.	St. Dev
0	112.4	P1	100.6	85.8	28.45	64.05	P1	59.98	100.0	13.74
		P2	5270	14.2	715.2		P2	-	-	-
7	190.1	P1	176.7	70.1	45.75	69.89	P1	63.18	100.0	12.24
		P2	5448	29.9	639.0		P2	-	-	-
14	517.8	P1	472.4	52.0	118.0	71.58	P1	68.22	100.0	13.82
		P2	5341	48.0	688.4		P2	-	-	-
21	843.3	P1	642.1	42.3	155.6	77.58	P1	71.59	100.0	18.69
		P2	5281	57.7	711.8		P2	-	-	-
28	2973	P1	1281	27.3	180.9	99.26	P1	89.30	100.0	18.72
		P2	5599.6	72.7	814.3		P2	-	-	-
35						115.9	P1	111.0	100.0	27.37
							P2			
42						158.1	P1	162.1	100.0	34.87
							P2			
49						174.4	P1	174.5	100.0	46.38
							P2	-	-	-
56						190.5	P1	189.6	100.0	48.19
							P2	-	-	-
63						294.7	P1	318.4	79.0	90.93
							P2	5443	21.0	640.4

Table 4 and Figs. 4 a and 4 b compare the DLS data on the two oils containing 6 % NPs. The first part is for oil without dispersant while other part of the Table (bold letters) is for oil with dispersant.

Observations for dispersant- free oil (DFO)

It was observed that with increase in time, tendency of agglomeration of NPs increased for both the oils viz. dispersant stabilized oil (DSO- O_{DN6}) and dispersant-free oil (DFO- O_{N6}). The extent, however, differed. For DSO, it was slow right from the beginning while for DFO it increased disproportionately faster. When DFO was freshly prepared, average particle size (APS) of major portion (86%) was \approx 100 nm while remaining portion was of 5270 nm indicating heavy agglomeration of particles in spite of extensive sonication. 100 nm size was higher than the original claimed size of NPs (\approx 50-70 nm) indicating it is extremely difficult to de-agglomerate the all the NPs if added in higher %. After 7 days, APS increased to 176 nm from 100 nm and other portion increased to 5448 nm from 5270 nm indicating re-agglomeration of NPs with time. After 14 days the rate of agglomeration was almost 5 times more. With further increase in time, portion of smaller particles decreased rapidly while that of bigger ones increased. After 28 days the agglomeration was so high that average particle size was 1181 nm (27 %) and bigger ones were 5600 nm (73 %). Thus it was concluded that without dispersant, NPs cannot stay in suspended form for extended time.

Observations for dispersant stabilized oil (DSO)

For DSO, beneficial effect due to dispersant was clearly seen. APS was 64 nm (100 % portion) indicating efficient de-agglomeration of NPs with the help of dispersant. After 7 days, APS slightly increased to 70 nm for 100 % portion. After 14, 21 and 28 days, NPs in oils were still in excellent condition (de-agglomerated) showing APS as 68, 72 nm and 90 nm respectively. There was no secondary peak indicating excellent performance of a

dispersant. After 35, 42, 49 and 56 days, slight agglomeration started. APS increased slightly to 110, 162 175 and 190 nm respectively. The secondary peak was still absent indicating very satisfactory condition of oil after almost 2 months. After 63 days, however, oil started showing heavy agglomeration indicating efficiency of dispersant to hold the NPs was limited for approximately 2 months only.

3.2 SRV Test-For Oils with only Dispersant

Tribo-performance of O_P was compared with that of O_D , O_{D5} and O_{D10} (Fig. 5a and 5b for friction and Fig 6 for wear).

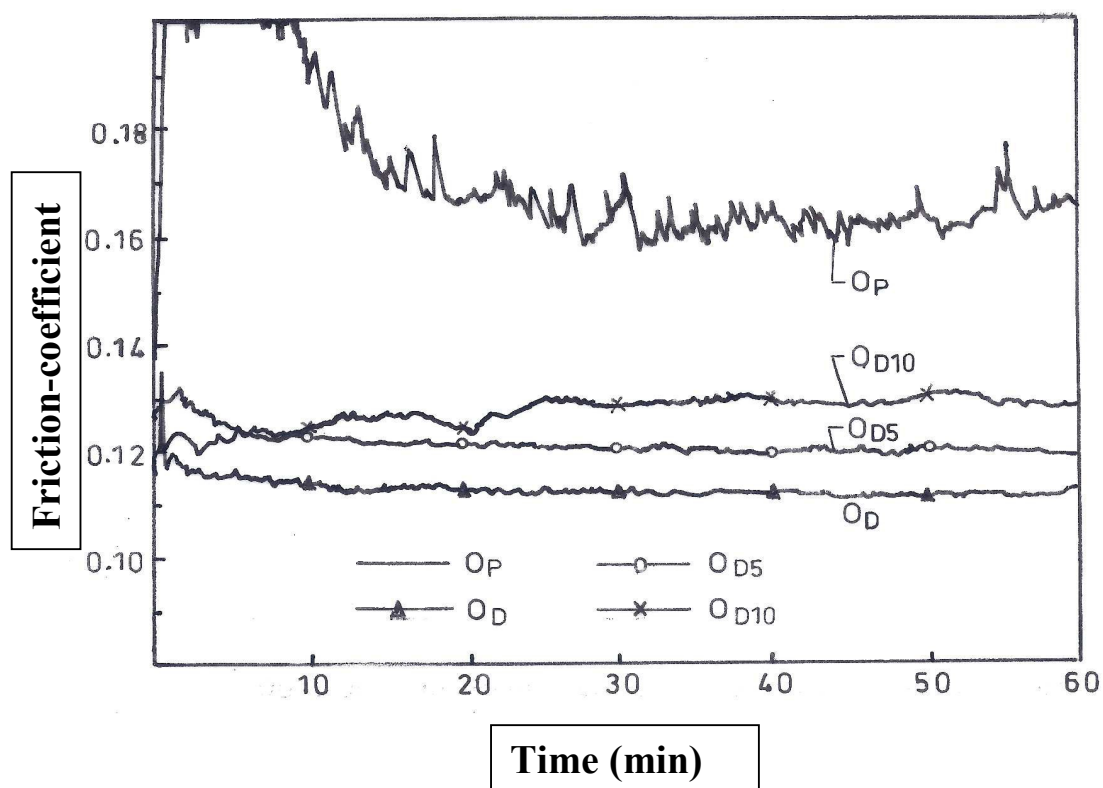


Figure 5a Friction coefficient as a function of fretting duration for selected oils (stroke- 1 mm, frequency- 50 Hz, Temp-50 °C, load 100 N and duration 1 hr).

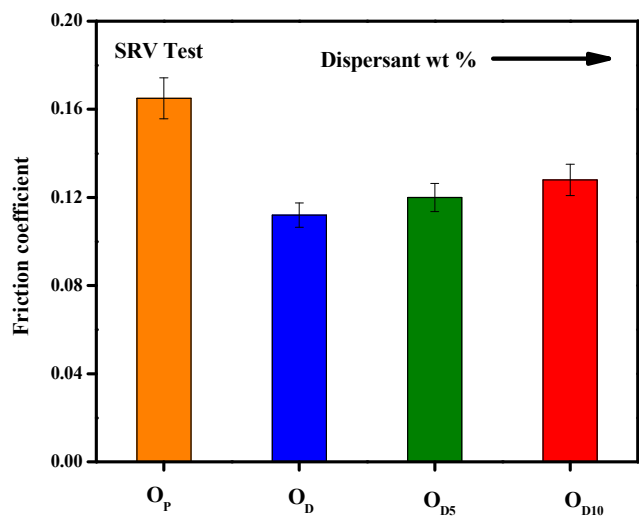


Figure 5b Comparison of coefficient of friction as a function of amount of dispersant.

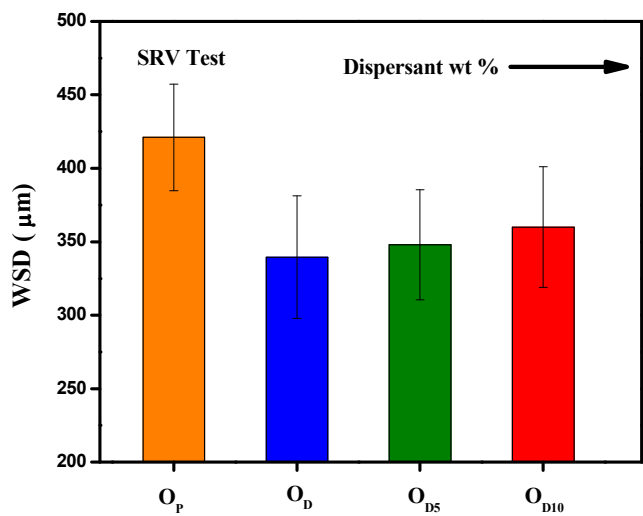


Figure 6 Comparison of wear scar diameter (WSD) as a function of amount of dispersant.

From Figs. 5 and 6 it was clear that inclusion of dispersant showed reduction in the μ and its fluctuations apart from reduction in wear scar diameter (beneficial effects). With increase in

amount, however, benefits reduced slowly confirming that 1 % was optimum amount for best friction and wear performance.

3.3 SRV Test-For Oils with Dispersant and nano-PTFE

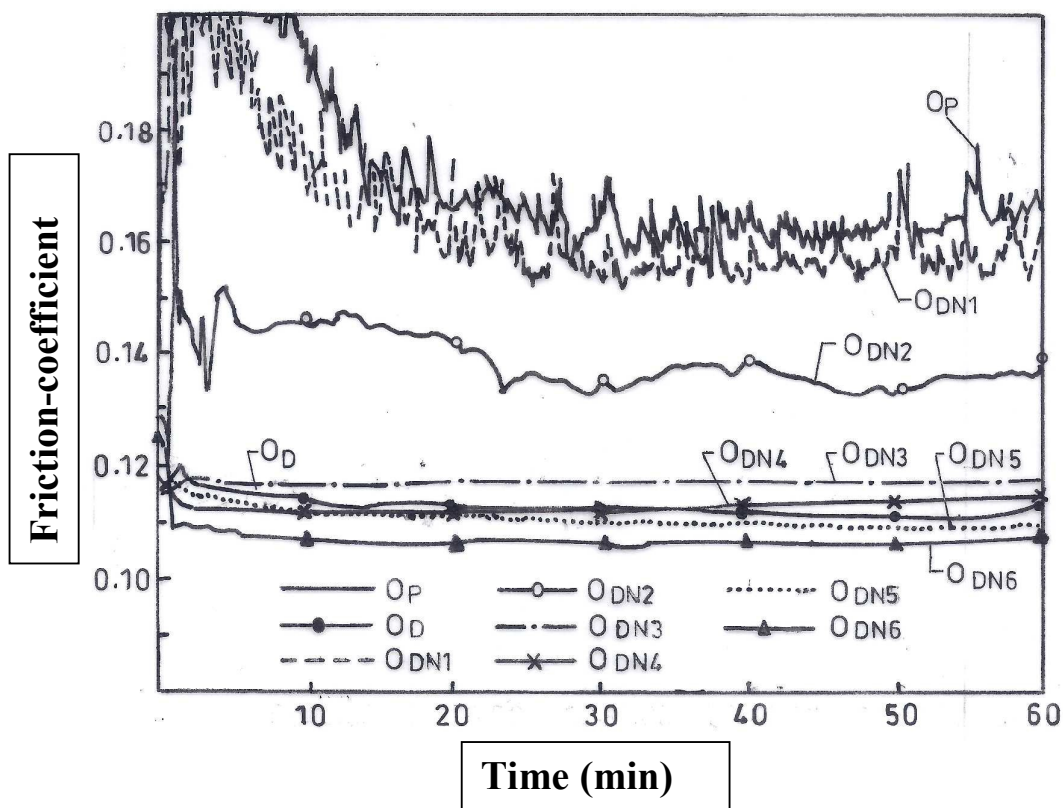


Figure 7a-Friction coefficient as a function of fretting duration for selected oils (stroke- 1 mm, frequency- 50 Hz, Temp-50 °C, load 100 N and duration 1 hr).

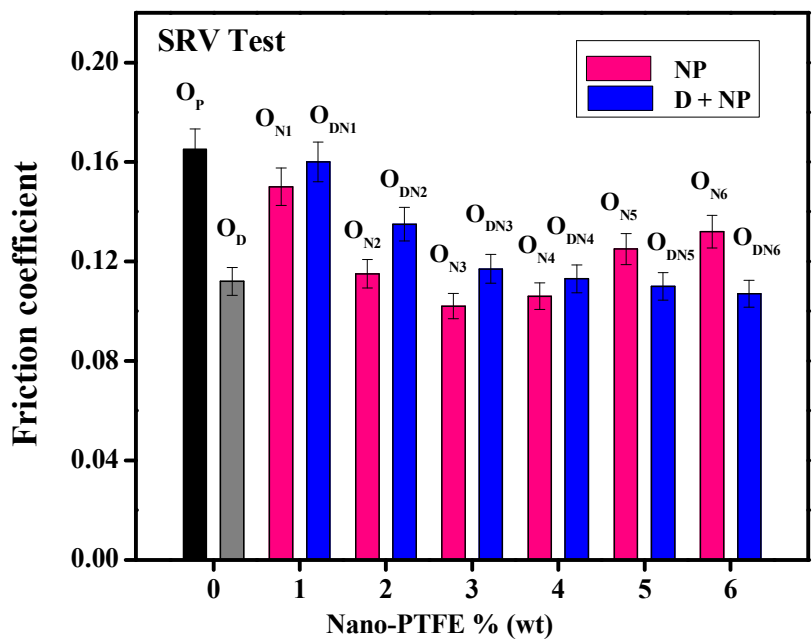


Figure 7b- Friction coefficient for selected oils at 100 N load (Part of data (pink bars) already published elsewhere [17]).

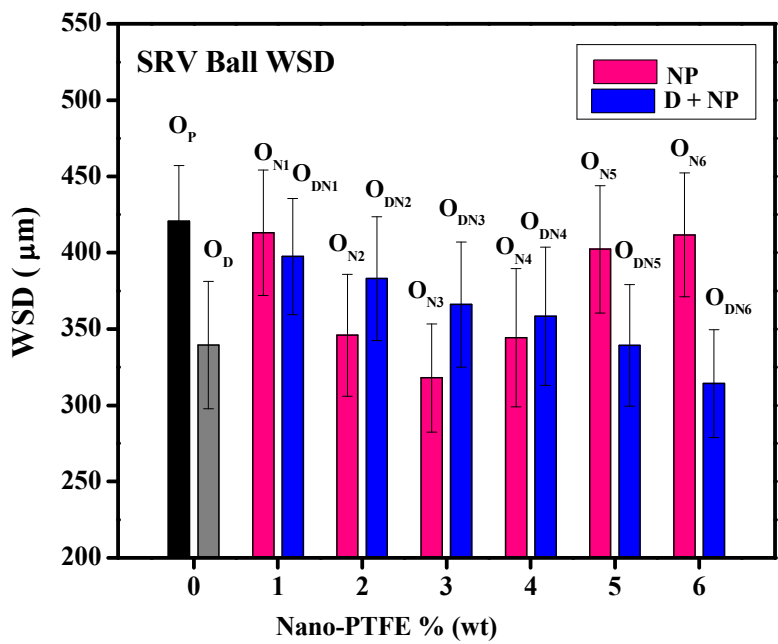


Figure 7c- Influence of concentration of nano-PTFE on wear scar diameter (WSD) of oils under 100 N load (Part of data (pink bars) already published elsewhere [17].

As observed from Fig. 7 from μ -fluctuations point of view O_{DN1} proved worst followed by O_p indicating initial antagonistic effect of combination of dispersant and 1 wt % NPs. O_{DN2} was the third in the series in this aspect indicating initiation of slow synergism in the performance, which then continuously improved as % of NPs increased. Interestingly, in the case of magnitude of μ (Fig 7b) O_D showed large reduction (32 %) in μ with respect to O_p , indicating dispersant itself acted as anti- frictional (AF) additive in oil. Inclusion of 1 % NPs to the O_D initially increased the μ sharply (from 0.175 to 0.225), which was just 7 % lower than that of a parent oil showing complete incompatibility of the two additives. It clearly indicates the competition between the two for beneficial layer formation on the surfaces, which led to the antagonistic effect. With increase in amount of NPs, however, this effect diminished slowly and PTFE particles became more dominant in controlling the μ to the extent that the μ O_{DN5} was identical to O_D . Furthermore, O_{DN6} showed the lowest μ in the series 0.107. It reduced the μ of parent oil by 35%.

The dispersant had to be added to increase the stability of nano-suspension and antagonism arising out of competition to layer formation had to be combated with 6 wt % NPs which finally was most effective in controlling the μ of O_D .

In earlier series 3 wt % NPs had exhibited lowest μ . Further increase in NPs led to slight reduction in benefits. It was argued that beyond 3 % NPs start agglomerating and number of NPs available for beneficial film formation reduce in spite of total amount of PTFE in oil (6 wt %). For new oils, dispersant was helpful to accommodate more particles of PTFE as NPs in oils and also enhancing the stability of nano-suspension for more time. However, this was at the cost of competitive role of dispersant as AF for film transfer with PTFE.

O_{N3} still remained as the best candidate to exhibit the lowest μ , though the difference was marginal when compared with new oils viz. O_D and O_{DN6} .

Figure 8c shows the variation of the wear scar diameter (WSD) with addition of varying concentrations of NPs in the dispersant added parent oil.

All the developed oils performed better than the virgin oil. It can be clearly seen that the best AW property was shown by O_{DN6} . Dispersant also acted as a powerful AW additive (19 % reduction in wear as compared to the parent oil). The moment NPs were added, antagonism in functioning of two additives started. It was highest for O_{DN1} , which slowly diminished with increase in amount of NPs. As the amount of NPs increased beyond 4 wt %, AW performance of the oils improved by the dominance of NPs and 25 % improvement was observed for O_{DN6} as compared to 19 % for O_D . Friction and wear performance of O_{DN5} and O_D was identical. Further increase in NPs (6 %) led to noticeable decrease (7 %) in wear as compared to O_D .

Overall performance improvement in AW property at 100 N load was as follows.

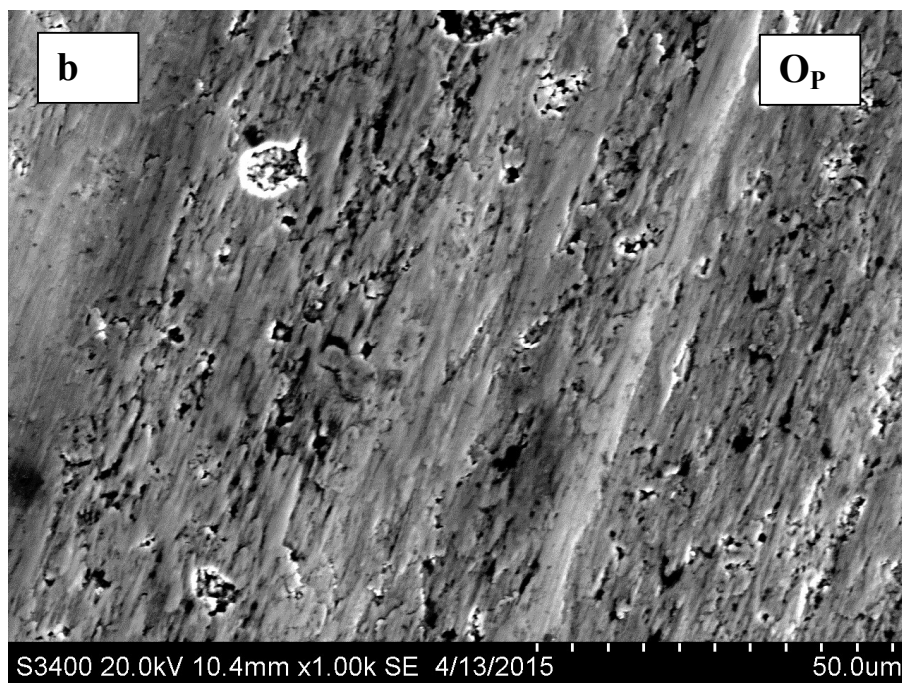
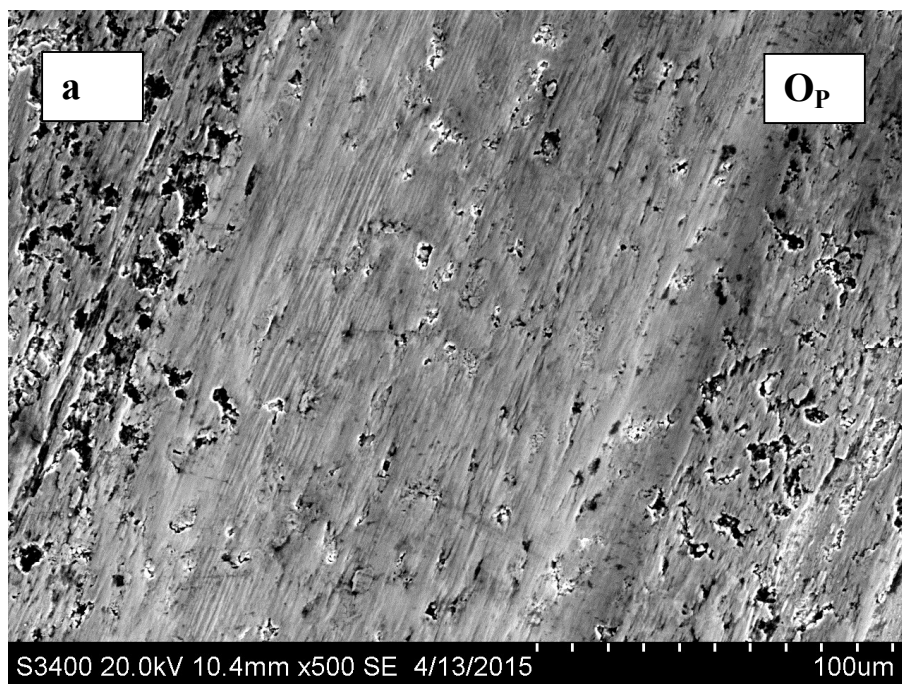
O_{DN6} (25 %) > O_{DN5} (19 %) > O_D (19 %) > O_{DN4} (15 %) > O_{DN3} (13%) > O_{DN2} (9 %) > O_{DN1} (6 %) > O_P .

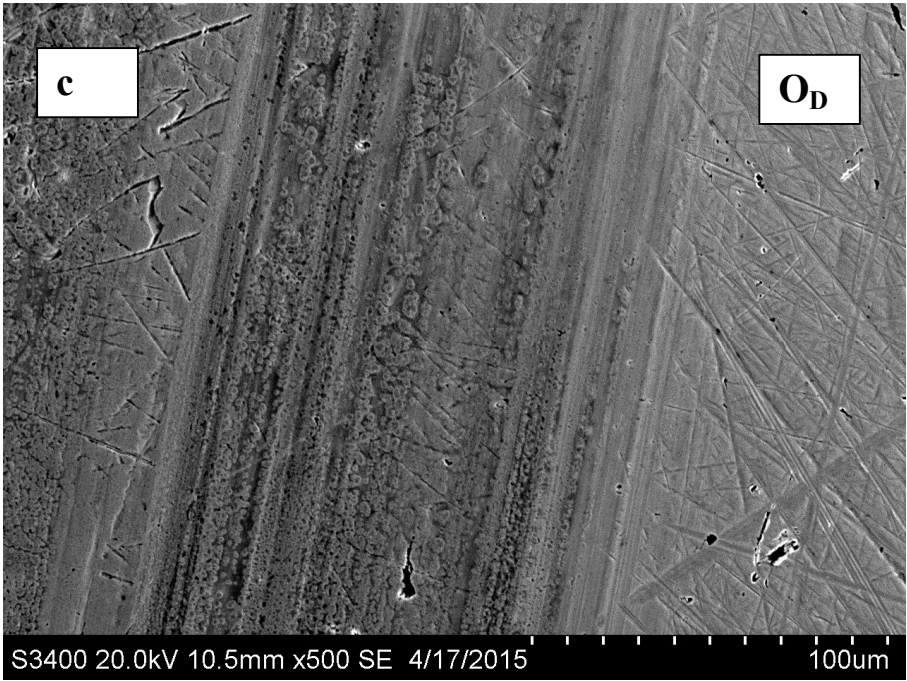
Comparative trends in performance of new oils and old oils also indicated similarity with friction studies.

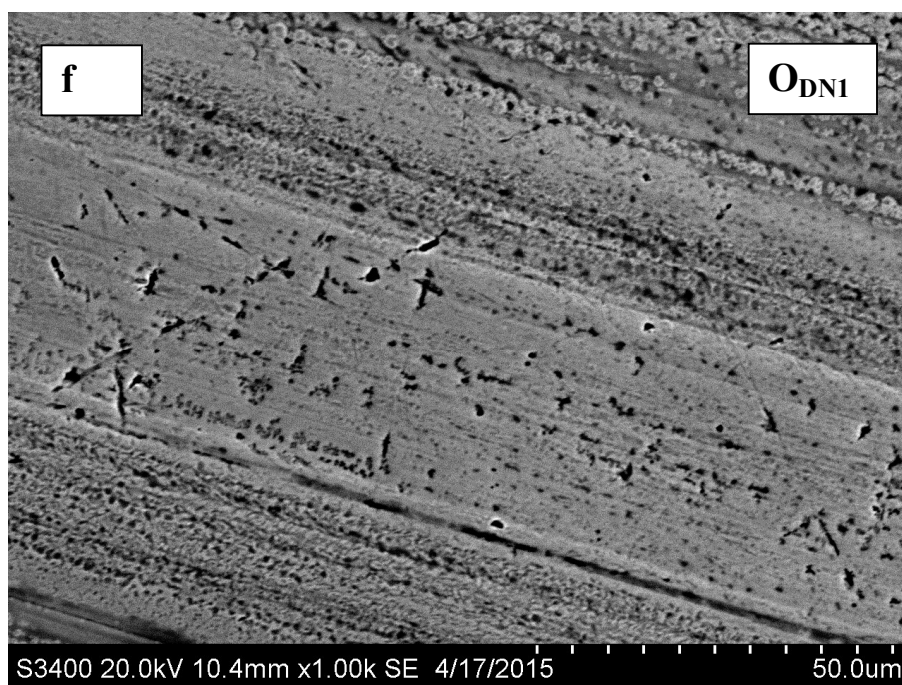
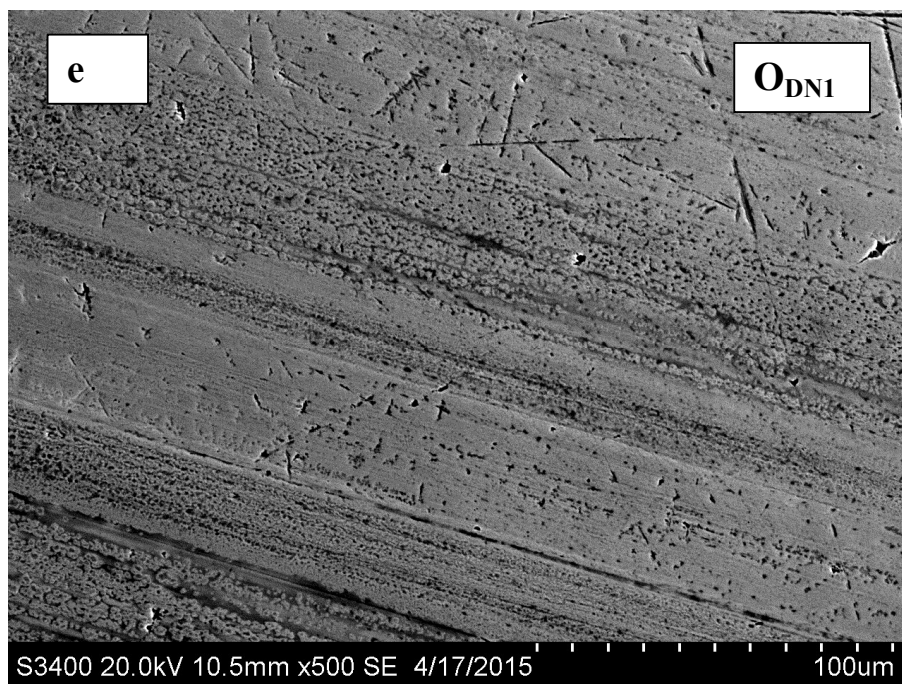
3.5 SEM-EDAX and AFM Studies on Worn Surfaces

3.5.1 SEM-EDAX Studies on worn disc surfaces

SEM studies were done on the worn surfaces to correlate the surface topography with wear trends. This is a supporting technique and did not reveal quantitative aspects. Figure 8 shows the micrographs of the worn surfaces of the steel disc lubricated with different NP-oils.







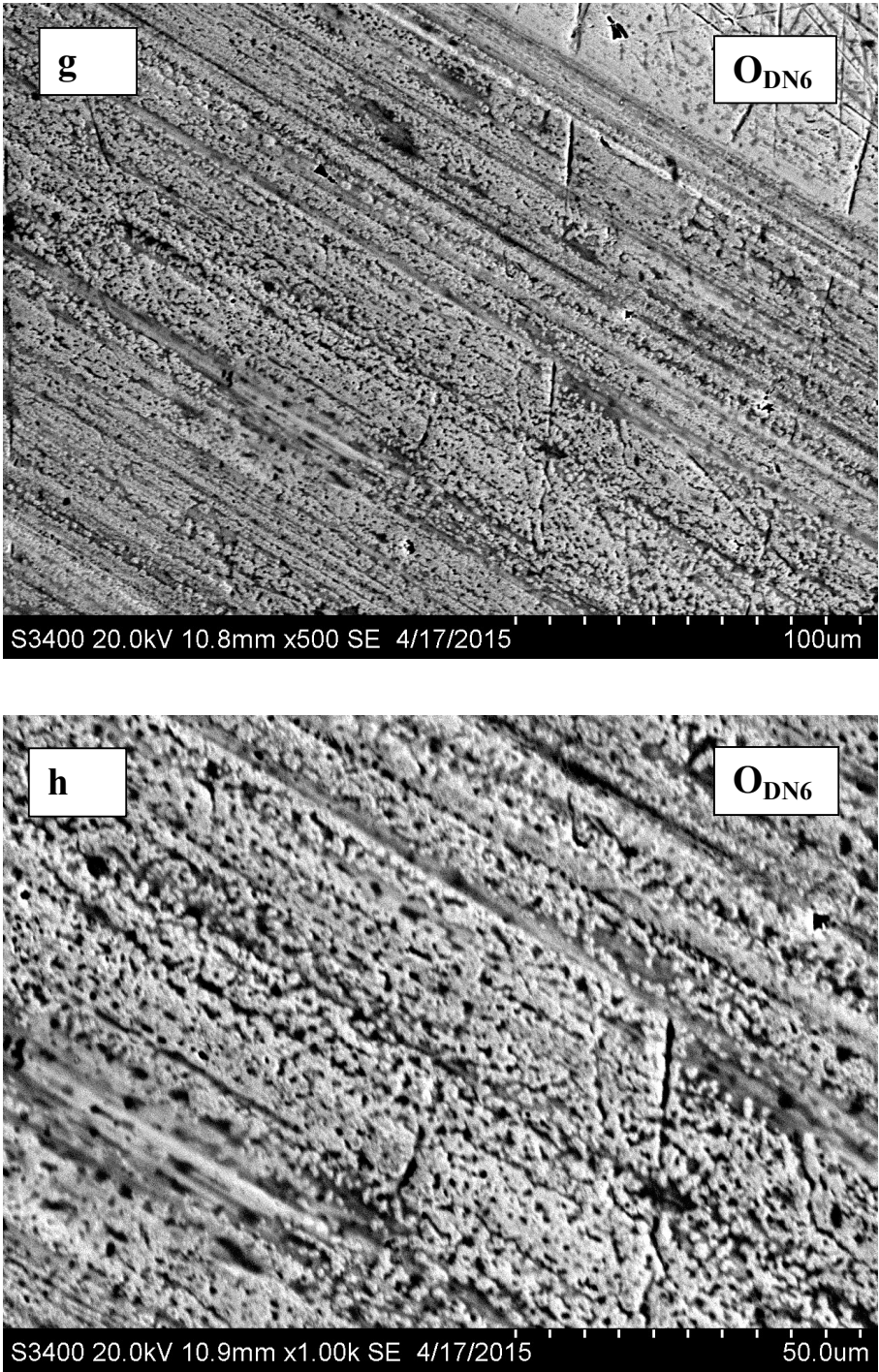


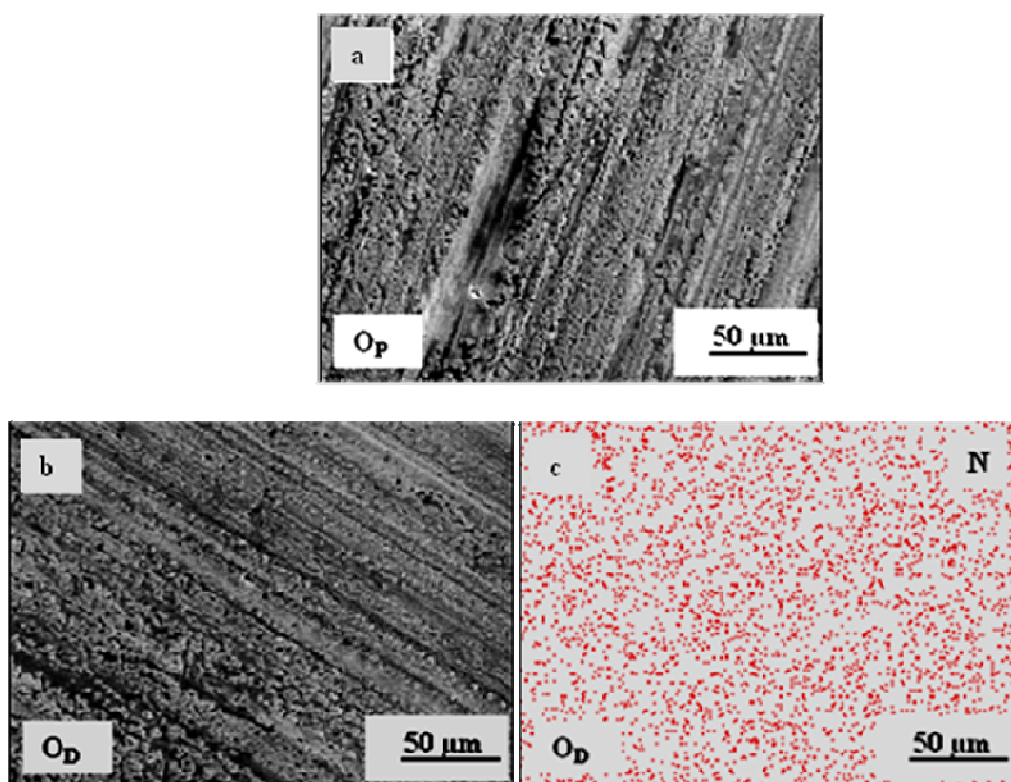
Figure 8 -SEM image of steel discs worn in various oils at 100 N load.

The efforts were made to examine if the trends in tribo-performance of oils and topography of worn surfaces showed some correlation. The SEM technique describes mainly the topography of surfaces qualitatively and is used in the literature as a supporting technique and not a confirmatory one. The reduction in μ and wear due to inclusion of dispersant/nano PTFE in the parent oil was correlated qualitatively with SEM observations. As seen in Figs. 8 a and 8 b, even after fretting for one hr. in parent oil, the surface was rough along with many thick and deep furrows. On the contrary, surface fretted in O_D (Fig. 8 c and d) was much smoother compared to that with O_P indicating the beneficial film formation which might have reduced the direct contact of asperities leading to reduction in friction and wear. In Fig. 8 e and f, in spite of presence of NPs, the texture of the film was not as smooth as in earlier case. The deterioration in the quality of film indicated antagonistic behaviour between nano-PTFE and selected dispersant. The texture of film continued to improve as PTFE concentration in oils increased. In the case of O_{DN6} , the film is distinctly more uniform, coherent and indicative of material transfer.

For better understanding of chemical nature of film, SEM and EDAX studies on the wear tracks on steel discs were done to have some idea of composition of transferred film and micrographs are collected in Fig 9. Micrographs are shown in Fig. 9a, 9b, 9d and 9h while their corresponding dot maps are shown in remaining micrographs.

The micrograph 9a is for the surface topography of oil (O_P) lubricated disc which showed some film transfer. EDAX studies showed the presence of Fe and not N or F (Dot maps for Fe were not included since Fe is present on every disc by default). On the contrary Fig. 9 (b and c) showed surface heavily covered with a third body. The tribo-layer of dispersant (Fig. 9c) was confirmed from the dot mapping of N (Nitrogen). This efficient film transfer protected the contact of metal surface leading to reduced friction and wear of the lubricant. For O_{DN1} and O_{DN6} there is uniform distribution of fluorine on the surfaces (9g) and (9k)

respectively. Also Carbon (9f) and (9j) were present on the worn surfaces of O_{DN1} and O_{DN6} respectively. Presence of carbon and fluorine confirms PTFE film on the wear scar. Presence of dispersant was confirmed by dot mapping of N (Nitrogen) (9e) and (9i) for O_{DN1} and O_{DN6} respectively. This transformed film protected the metal surface from asperity-asperity contacts. Being small in size NPs can easily enter into the valleys/crevices on the surfaces and they form the desirable film of a solid lubricant. For reduced friction and wear minimal asperity-asperity contact is desirable. Thin coherent film covering maximum asperity-asperity contact leads to improved tribological performance.



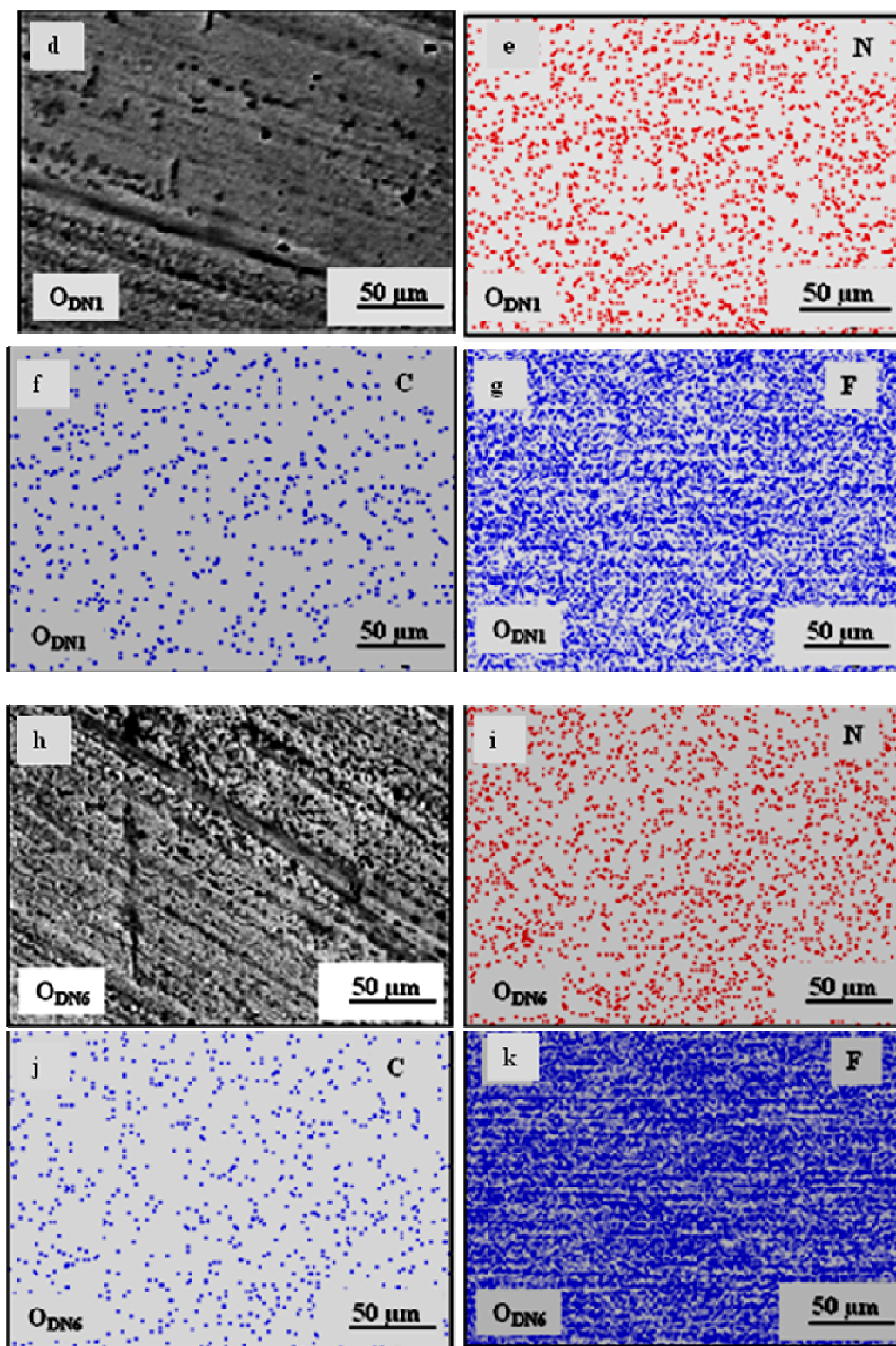


Figure 9- SEM micrographs and EDAX dot maps on worn steel discs (load-100 N, stroke- 1 mm, frequency- 50 Hz, Temp-50 °C and duration 1 hr); (a)- with lubricant O_P; (b and c)- with lubricant O_D confirming presence of dispersant traces in the transferred film; (d, e, f and g)- SEM micrograph , N, C and F dot maps on disc with

lubricant O_{DN1} and h, i, j and k)- SEM micrograph, N, C and F dot maps on disc with lubricant O_{DN6} confirming the transferred film contains both, dispersant and PTFE.

3.5.2 AFM Studies on the worn disc surfaces

AFM was used to study the topography of the wear track produced on the steel discs after the 60 minutes test at 100 N load. The three dimensional morphology of tracks produced during fretting in the presence of O_P , O_D , O_{DN1} and O_{DN6} are shown in Fig. 10. The images were taken in the wear track on the steel disc after sliding.

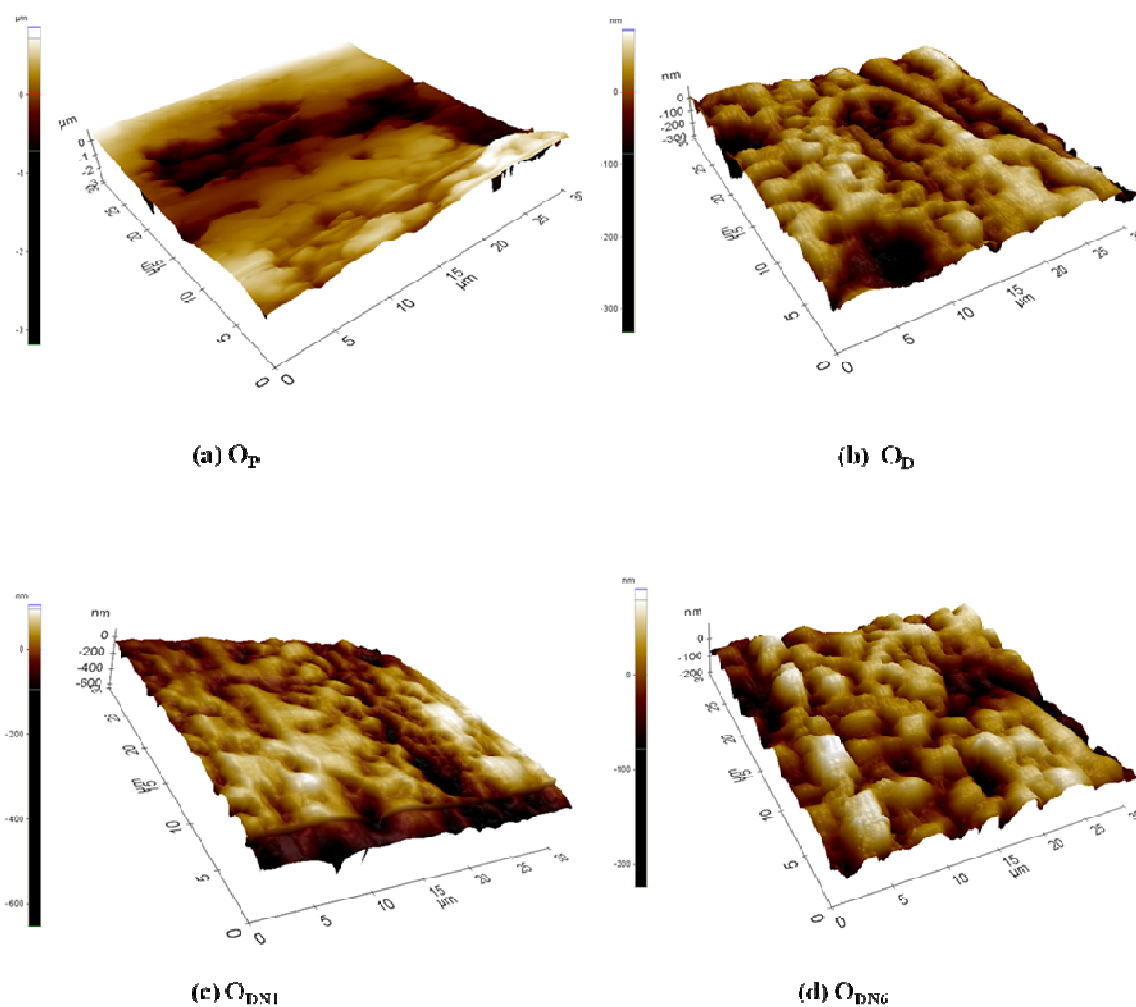


Figure 10-AFM images of the worn surfaces of the steel discs (load-100 N, stroke- 1 mm, frequency- 50 Hz, Temp-50 °C and duration 1 hr); (a) O_P , (b) O_D , (c) O_{DN1} and (d) O_{DN6} .

The AFM images of wear tracks for O_D , (b) O_{DN1} (c) and O_{DN6} (d) are different from that for O_P in Z direction. The topography of protruded portion or roughness of the surface for O_P is in microns while that for others is in nm units. This confirmed the significantly rougher characteristics of first surface related to O_P , which showed highest wear. Other surfaces showed pad-like structure and the tribofilm formed by the experimental NP-oils is an indication of good boundary film. Similar morphology for the additives that forms protective tribo-fims was studied elsewhere [21-26].

Figure 11 shows AFM deflection images and corresponding line profiles for steel disc surfaces worn in the presence of- O_P (a), O_D (b), O_{DN1} (c) and O_{DN6} (d). The roughness (Ra) values of the line profiles of O_P , O_D , O_{DN1} and O_{DN6} were listed in Table 5. The wear pattern was in the order; $O_P > O_{DN1} > O_D > O_{DN6}$.

It can be seen from the Table 5 that a surface roughness decreased with addition of dispersant and nano-PTFE. For O_{DN6} it was minimum (30 nm), while for O_P it was maximum (401nm). O_{DN1} showed higher Ra value (37 nm) than O_D (32 nm) which was accordance with wear pattern.

Table 5- The surface roughness (Ra) of line profile of the selected NP-oils.

	O_P	O_D	O_{DN1}	O_{DN6}
Ra (nm)	401	32	37	30

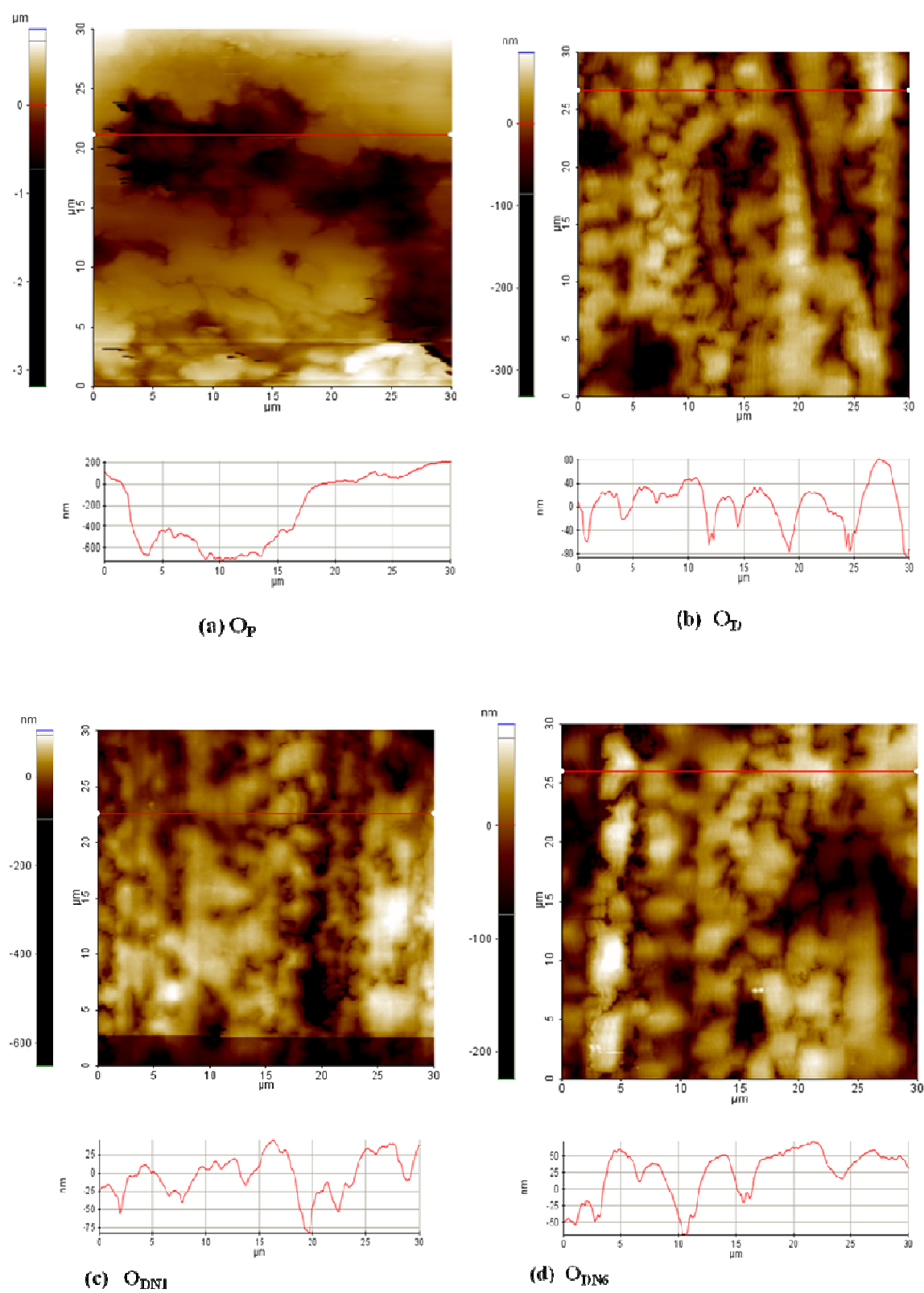


Figure 11-AFM deflection images and corresponding line profiles for steel surfaces; (a) O_P , (b) O_D , (c) O_{DN1} and (d) O_{DN6} .

4. Conclusions

In this paper, the effect of nano-PTFE- PIBSI additive interaction in a lubricant system is reported. The NP-oils (using nano-PTFE as additive) developed in earlier work had shown significant enhancement in performance properties. However, they suffered from a stability issue and NPs started settling down after 15 days. It was necessary to enhance the stability with the help of dispersant. Hence 1 % PIBSI was added as dispersant and results of simultaneous interaction of two additives in oil are reported in this paper

We had also reported in earlier paper that beyond an optimal concentration (3 %), NPs did not enhance the performance and inefficient de-agglomeration of NPs was offered as a reason for this phenomenon. However, hardly any evidence was given for supporting this hypothesis. In this paper we have come up with the evidence, which is definitely a significant addition to the science of oils with nano-solid lubricants.

Inclusion of PIBSI (1 %) in NP-oils enhanced the stability of nano-suspension significantly. Till 2 months there was no indication of sedimentation as confirmed from the visual inspection and DLS (dynamic light scattering) studies. The dispersant itself proved to exhibit very good anti-friction and anti-wear properties. Amongst selected amounts (1, 5 and 10 %), 1 % was found to be optimum for the best tribo-properties. The tribo-properties of the oils containing both the additives (dispersant and nano-PTFE), however, were affected adversely due to the dispersant. The performance (both friction and wear) decreased when nano-PTFE was added in low amount. It was due to the competition of film transfer on the counterface by both the additives. As a net result hardly any good uniform, and beneficial film could be transferred. With increase in amount of PTFE, however, this antagonism problem diminished to the extent that oil with 6 % NPs stabilised by 1 % PIBSI showed lowest friction and wear.

In the case of nano-PTFE without dispersant 3 % NPs were observed to be optimum amount for significantly enhanced performance. When compared with the new oils with dispersant and NPs, 6 % proved the best since more NPs were in de-agglomerated form, which was not

possible without PIBSI. The performance of NP-oils without dispersant was always significantly better than those with dispersant. Finally it was concluded that the stability to the nano-suspension was achieved by adding PIBSI, but at the cost of some initial loss in the tribo-performance.

The paper should be of interest to the researchers and practitioners in the area of formulations of finished-oils, lubricants and additives, nano-particles, polymeric materials and their interaction with metallic surfaces. In depth analysis of the interacting surfaces by scanning electron microscopy/ atomic force microscopy showed film transfer on the counter face. However, further studies are needed to fully quantify the structure and thickness of these tribo-films.

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